"Kinetic Studies of Nonequilibrium Plasma-Assisted Combustion"

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This project focuses on an integrated experimental/modeling study of hydrocarbon oxidation mechanisms under conditions of extreme thermal non-equilibrium. Large, and highly non-equilibrium, initial pools of important hydrocarbon combustion intermediate and electronically excited air species are created in a short pulsed fuel-air plasmas, created using ~10-20 nsec duration – high (~20 kV) voltage pulsers, capable of operation at repetition rates as high as 40-50 kHz. The time evolution of critical species and temperature, after application of a single nanosecond discharge pulse, or a rapid "burst" of pulses, depending upon the experiment, are experimentally determined using advanced laser-based optical diagnostic methods. Results are compared to theoretical predictions from discharge and plasma chemical kinetic codes, developed as part of this program, in order to provide model validation and to improve understanding of fundamental nonequilibrium plasma kinetics in air and air/fuel mixtures.

Summary of Accomplishments

The following five major accomplishments were the direct result of funding provided by this program.

i. Two Photon Laser Induced Fluorescence (TALIF) studies of atomic oxygen creation and loss kinetics in air, methane/air, and ethylene/air nanosecond pulsed discharges.
ii. Pure Rotational Coherent Anti-Stokes Raman Spectroscopy (CARS) studies of oxidation and heat release in ethylene-air nanosecond pulsed discharges.
iii. Single photon Laser Induced Fluorescence (LIF) studies of NO creation and lost kinetics in air, methane/air, and ethylene/air nanosecond pulsed discharges.
iv. Pure rotational Coherent Anti-Stokes Raman Spectroscopy (CARS) studies of oxidation, heat release, and ignition in hydrogen-air nanosecond pulsed discharges.
v. Development of a new, non-empirical model for nanosecond pulsed discharge plasma dynamics and energy coupling.

The most important findings from each of the above will be briefly summarized below. More detail can be found in the cited publications.

Experimental Apparatus

Figure 1 shows a simplified schematic of a 1-D pulsed discharge, optical access "flow" reactor that was used for the measurements performed for this program. The channel is 220 mm long x 22 mm width x 10 mm height, with 1.75 mm thick walls, and is constructed from a single piece of UV grade quartz. Measurements have been conducted in dry air and in mixtures of dry air with methane, ethylene, and hydrogen. Flow rates of air and fuel are controlled by mass flow controllers, at pressures in the range 40 – 100 Torr and flow velocity of approximately u=0.8 m/sec, corresponding to flow residence time in the discharge region of approximately 75 msec.

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14. ABSTRACT
This project focuses on an integrated experimental/modeling study of hydrocarbon oxidation mechanisms under conditions of extreme thermal non-equilibrium. Large, and highly non-equilibrium, initial pools of important hydrocarbon combustion intermediate and electronically excited air species are created in a short pulsed fuel-air plasmas, created using ~10-20 nsec duration – high (~20 kV) voltage pulsers, capable of operation at repetition rates as high as 40-50 kHz. The time evolution of critical species and temperature, after application of a single nanosecond discharge pulse, or a rapid "burst" of pulses, depending upon the experiment, are experimentally determined using advanced laser-based optical diagnostic methods. Results are compared to theoretical predictions from discharge and plasma chemical kinetic codes, developed as part of this program, in order to provide model validation and to improve understanding of fundamental nonequilibrium plasma kinetics in air and air/fuel mixtures.

15. SUBJECT TERMS
Plasma Assisted Combustion, Low temperature oxidation kinetics, discharge physics

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Two rectangular copper plate electrodes, 14 mm wide by 65 mm long, and are rounded at the corners to reduce the electric field nonuniformity, are attached to the outside of the quartz channel. Pulsed plasmas are produced by application of ~20 kV peak voltage - ~10-25 nanosecond pulses, using a variety of high voltage pulsed power supplies available in our laboratory, capable of operation at maximum repetition rates in the range 40 to 100 kHz. Laser beams are incident from either right or left, depending upon the experiment. A variety of detectors, filters, grating spectrometers / Optical Multi-Channel Analyzers, ICCD cameras are available for detection of LIF, TALIF, and CARS signals, as well as for imaging discharge structure.

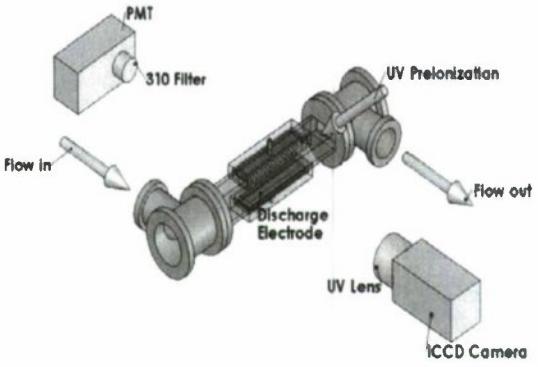

Figure 1. Schematic diagram of basic plasma assisted combustion test section.

Summary of Individual Studies

i. Two Photon Laser Induced Fluorescence (TALIF) studies of atomic oxygen creation and loss kinetics in air, methane/air, and ethylene/air nanosecond pulsed discharges.

This work is described in detail in Publications 2, 9 and 10. Summarizing the experiment very briefly, the TALIF diagnostic employs the well known atomic oxygen two photon allowed $2P\ ^3P$ - $3P\ ^3P$ absorption transition of at ~226 nm. Relative atomic oxygen concentration data is put on an absolute scale using the xenon-based optical calibration scheme of Niemi, et al [1,2].

Figures 2 and 3, which illustrate the most significant results, show absolute atomic oxygen mole fractions in air, Φ = 1.0 methane/air (Fig. 2) and Φ = 0.5 ethylene-air, at 60 torr and approximately 300 K as a function of time after initiation of a single, 20 nsec discharge pulse, along with plasma chemical modeling predictions. Note that the air data in Figs. 2 and 3 is identical, but plotted on linear (Fig. 2) and log (Fig. 3) scales to provide better comparison with the fuel data. It can be seen that in air oxygen atoms peak on a time scale of ~10-100 μsec after discharge initiation, due to collisions with nitrogen metastable molecules $N_2(A^3\Sigma) + O_2 \rightarrow N_2(X^1\Sigma) + O + O$, which accounts for approximately 75% of the total molecular oxygen dissociation produced by the pulsed discharge. Atomic oxygen loss in air is due to slow three body ozone formation, $O + O_2 + M \rightarrow O_3 + M$, which occurs on a time scale of several msecs.

From Fig. 2 it can be seen that in stoichiometric methane/air the rate of atomic production is essentially identical to that in air, and the loss rate is increased by a factor of approximately three. As discussed in _, in methane/air at room temperature the principal loss mechanism for atomic oxygen is reaction with methyl (CH_3) radicals, produced by both electron impact and dissociating collisions of methane with metastable N_2. Reaction with methane, at room temperature, is extremely slow. However, in ethylene/air mixtures, as shown in Fig. 3, the rate of decay of atomic oxygen is ~three orders of magnitude faster due to processes such as $O + C_2H_4 \rightarrow CH_3 + HCO$ and $O + C_2H_4 \rightarrow H + CH_2CHO$ which are fairly rapid (rate coefficient of ~

$k=4.9\cdot10^{-13}$ cm^3/s) at ~300 K. Modeling results prediet that rapid reaction of O atoms and ethylene initiates a series of exothermie low temperature oxidation ehemistry, resulting in substantial heating (~500-700 °C) and, in some eases, ignition.

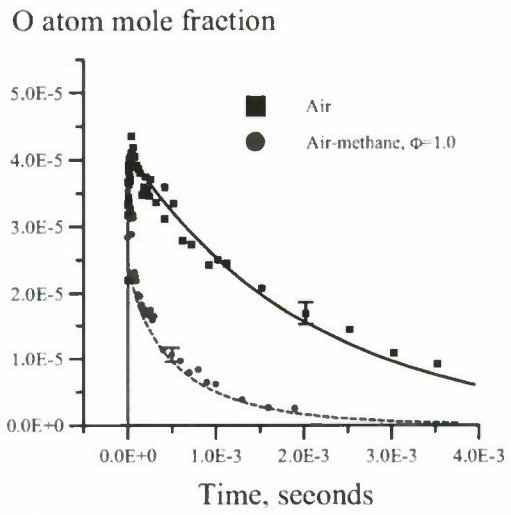

Figure 2. Oxygen atom mole fraction vs. time after a single high-voltage pulse in air and in a methane-air mixture at P=60 torr and Φ=1.0.

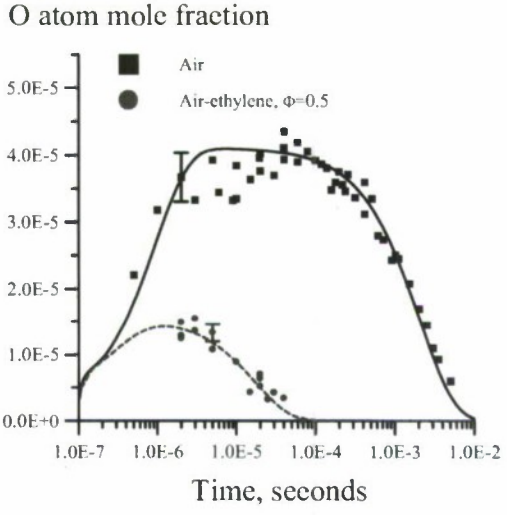

Figure 3. Oxygen atom mole fraction vs. time after a single high-voltage pulse in air and in an ethylene-air mixture at P=60 torr and Φ=0.5.

ii. Pure Rotational Coherent Anti-Stokes Raman Spectroscopy (CARS) studies of oxidation and heat release in ethylene-air nanosecond pulsed discharges.

While measurement of the temporal evolution of speeies mole fraction after initiation of a single discharge pulse, such as those summarized in Figs. 2 and 3 above of have served to validate modeling predictions for key low temperature plasma oxidation processes, because the energy coupled to the plasma by a single nanoseeond pulse is fairly low (of the order of ~0.1 mJ/cm^3/pulse or ~0.1 meV/moleeule/pulse), detectable heat release requires from a few tens to a few hundred pulses generated at a high pulse repetition rate (~10-100 pulses/msec). To address this need a major aetivity of the current program has been to assemble a new, to our laboratory, pure rotational Coherent Anti-Stokes Raman Spectroscopy (CARS) instrument and to use it for a series of measurements of rotational-translational temperature rise in air, ethylene-air, and

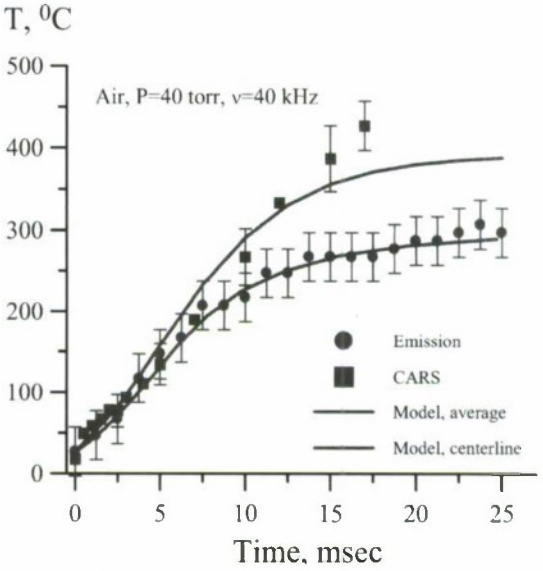

Figure 4: Comparison of experimental spatially averaged (emission) and centerline (CARS) temperatures in a repetitively pulsed nanoseeond discharge in air at P=40 torr with plasma ehemistry model prediction.

hydrogen-air mixtures, excited by "bursts" of 10 to approximately 600 high voltage, nanosecond duration pulses, at 40 kHz pulsed repetition rate.

Figures 4 – 6 summarize the most important findings for ethylene-air mixtures, more details of which can be found in publication _. Figure 4 shows time resolved air plasma temperatures inferred from both N_2 second positive emission spectroscopy and CARS, along with plasma chemistry model predictions for a pulse burst discharge at P=40 torr and 40 kHz pulse repetition rate. Both emission (i.e. spatially averaged) and CARS (centerline) temperatures are very close to each other until approximately 7.5 msec (300 pulses). After this time, the emission temperature rise becomes slower and starts to level off, indicating significant heat transfer losses, while the CARS temperature continues to increase up to 17 msec (680 pulses). At t=15 msec (600 pulses), the difference between CARS and emission temperature is about 100^0 C. Note that the plasma kinetic model assumes a constant wall temperature of T_w=300 K, which appears to adequately describe the transverse temperature distribution in the air plasma.

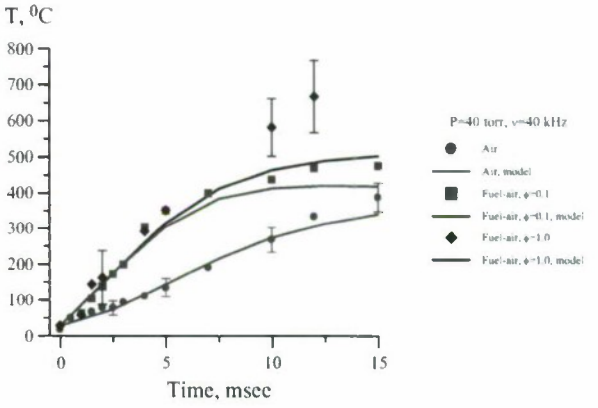

Figure 5: Comparison of experimental centerline (CARS) temperatures in a repetitively pulsed nanosecond discharge in air and in ethylene-air (Φ=0.1 and Φ =1.0) at P=40 torr with the plasma chemistry model prediction.

Figure 5 compares the CARS temperature with the centerline temperature predicted by the kinetic model in air, lean (φ=0.1), and stoichiometric (φ=1.0) ethylene-air mixtures at P=40 Torr and a burst repetition rate of 40 kHz. Both experimental and predicted temperatures are plotted as functions of discharge burst duration. A few general trends are clearly observed. First, comparison of experimental temperatures in air and ethylene-air show that the rate of temperature rise in both fuel-air mixtures is much faster than in air during the first 5 msec (200 pulses), approximately 350^0 C verses 125^0 C. Second, the CARS data show that during this stage the rates of heat release in lean and stoichiometric ethylene-air mixtures are very close to each other, although the fuel mole fractions differ by a factor of 10. Third, experimental temperatures in air and in the lean ethylene-air mixture reach a quasi steady-state at t~15 msec (600 pulses), while temperature in the stoichiometric ethylene-air mixture continues to rise.

Two of these trends are well reproduced by the kinetic model. In particular, the model predicts a significantly more rapid centerline temperature rise in air-fuel mixtures than in air, consistent with the CARS data. Also, predicted rates of centerline temperature rise in air-fuel mixtures at φ=0.1 and 1.0 are very close to each other until t=5 msec. However, the model predicts a significantly lower temperature in the stoichiometric air-fuel mixture at t>5 msec than is measured experimentally. Specifically, the model predicts that by 5 msec (200 pulses) the temperature reaches a quasi steady-state, whereas the CARS data indicates that it continues to rise. To explain these general trends, it is noted that the rate of heat release in the plasma as a function of number of pulses in the burst depends significantly on mixture composition. Figure 6, which plots atomic oxygen and ethylene mole fractions predicted by the plasma kinetic model in air, and φ=0.1 and 1.0 mixtures (i.e. at the conditions of Fig. 2), provides some insight into

these trends. In the absence of fuel, O atoms formed during, and immediately after, the discharge pulse decay relatively slowly in recombination reactions, $O + O_2 + M \rightarrow O_3 + M$ and $O + O_3 \rightarrow 2O_2$. In air, the relatively low rate of recombination results in a considerable build-up of O atoms, to mole fractions of up to ~1%, which is comparable to the 0.7% initial mole fraction of ethylene in the lean air-fuel mixture (φ=0.1). However, in ethylene-air mixtures, O atoms rapidly react with ethylene due to the parallel processes, $O + C_2H_4 \rightarrow CH_3 + HCO$ and $O + C_2H_4 \rightarrow H + CH_2CHO$, both of which are relatively fast at low temperatures. These low-temperature reactions of atomic oxygen with ethylene initiate a number of net exothermic hydrocarbon reactions, resulting in accelerated temperature rise, which the model accurately predicts, as can be seen in Fig. 5.

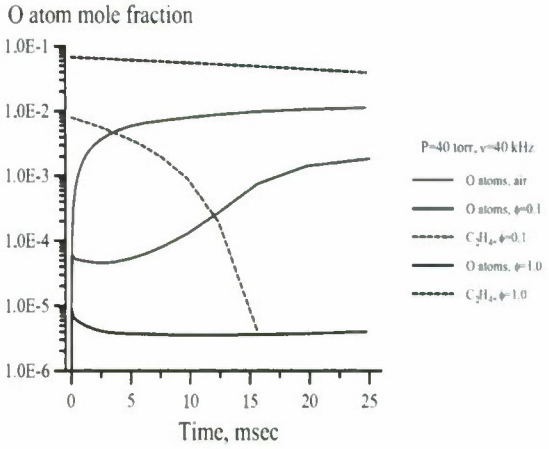

Figure 6: Plasma chemistry model predictions for O (solid curves) and ethylene (dashed curves) mole fractions for air and ethylene-air mixtures.

Because of these rapid reactions with ethylene, O atom number densities in ethylene-air mixtures are much lower than in air under otherwise identical conditions. This can be seen by comparison of the solid red (air) and black (ethylene-air, Φ=1) curves in Fig. 6. Further, as long as fuel is in excess, the rate of chemical energy release (and therefore the rate of temperature rise) in air-fuel mixtures is dictated by the rate of O atom generation, which is only slightly affected by the ethylene mole fraction in the mixture (0.7-6.5%). For this reason, the predicted initial heating rates in the lean and stoichiometric ethylene-air mixtures are very close to each other, which is again consistent with the experimental CARS temperature measurements shown in Fig. 4. After nearly all fuel in the lean mixture has been oxidized (after ~200 discharge pulses, or ~5 msec), the heating rate is predicted to slow down, and, simultaneously, the O atom number density is predicted to start rising rapidly. However, since the stoichiometric mixture has ten times more fuel, its mole fraction remains approximately constant (dashed black curve in Fig. 3), as does the corresponding predicted heating rate. For this reason, the stoichiometric mixture continues to generate additional heat as the number of pulses increases beyond ~200–400 (5–10 msec). The most likely reason for the significant difference between experimental and predicted centerline temperatures in the stoichiometric mixture after large number of pulses (~400 pulses, or ~10 msec) is heating of the test section walls. At these conditions, the use of the constant wall temperature boundary condition (T_w=300 K) is likely no longer justified, since the rate of heat transfer from the plasma to the cold wall is significantly overestimated.

This work is described in more detail in Publications 5 and 14.

iii. Single photon Laser Induced Fluorescence (LIF) studies of NO creation and lost kinetics in air, methane/air, and ethylene/air nanosecond pulsed discharges.

While NO production and destruction in non-equilibrium plasmas has traditionally been studied from the perspective of pollutant mitigation, it can also play a role in low temperature oxidation due to the process $HO_2 + NO \rightarrow NO_2 + OH$. This provides both a low temperature means of producing OH, with subsequent highly exothermic H abstraction, $RH + OH \rightarrow R + H_2O$, and a

means to mitigate a key low temperature ehain termination proeess. Indeed, it has been observed in equilibrium low temperature flow reactor studies by Bromley, et al.,[3], that traee (a few ppm) quantities of NO aeeelerate low temperature(~650-700 K) oxidation of butane.

To study the implieations of this for nonequilibrium PAC, NO studies were performed using the well known single photon X ($^2\Pi$) → A ($^2\Sigma^+$) LIF transition at ~ 226 nm. Note that this is very elose to the atomie oxygen TALIF absorption, enabling the use of an essentially identieal experimental apparatus. Principal results of these studies in air are summarized in Figs. 7 and 8. Figure 7 shows experimental data (blaek eireles), as well as modeling predietions for NO and a number of other key speeies using a "baseline" air plasma model eonsisting of a set of ordinary differential equations for number densities of a large number of neutral and eharged speeies produeed in the plasma, as well as the energy equation for predieting the temperature of the mixture. This set of equations is coupled with the steady, two-term expansion Boltzmann equation for the eleetron energy distribution funetion (EEDF) of the plasma eleetrons, using experimental eross seetions of eleetron impaet eleetronie exeitation, dissoeiation, ionization, and dissoeiative attaehment proeesses. Full details are provided in publieation _. Foeusing on the solid blaek eurve in Fig. 7, it ean be seen that the baseline model prediets peak NO mole fraetion whieh is a faetor of ~four lower than that observed, and, more eritieally, a eharaeteristie time seale for peak NO eoneentration whieh is longer, by ~two orders of magnitude, than that observed experimentally (~250 mieroseeonds, experimental, vs 25 msee from baseline model). Note that the baseline prediction is dominated by the ordinary equilibrium Zeldovieh meehanism

$$N_2 + O \rightarrow NO + N \qquad (1a)$$
$$N + O_2 \rightarrow NO + O \qquad (1b)$$

whieh prediets very slow NO formation at low temperature. In addition, while not shown, time-resolved spontaneous emission measurements showed eonelusively that the N_2 ($C^3\Pi$), and $N_2(A^3\Sigma)$ exeited states deeay on time seales of 10-20 nsee, and 1-2 mieroseeonds, respeetively so that signfieiant NO formation via proeesses sueh as $N_2(A^3\Sigma) + O \rightarrow NO + N$ ean also not explain the observations in Fig. 7.

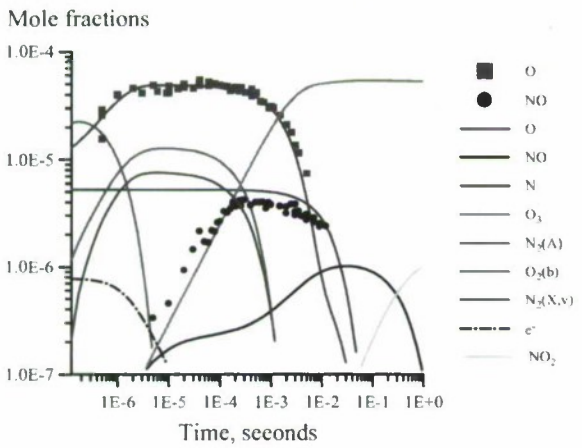

Fig. 7: Experimental O atom and NO eoneentrations (symbols) and speeies eoneentration predieted by the baseline model (lines) after a single-pulse diseharge in air. P= 60 torr.

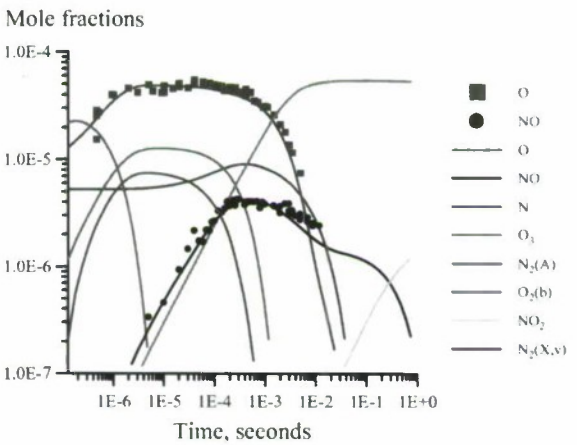

Fig. 8: Experimental O atom and NO eoneentrationd (symbols) and speeies eoneentration predieted by Model II ("N_2(v)" model, lines) after a single-pulse diseharge in air. P= 60 torr.

After a detailed analysis, documented in Uddi, et al, 2009 (Publieation 3), it was determined that the most likely proeess responsible for the observed rate of low temperature NO formation is the reaetion of highly vibrationally exeited ground eleetronie state N_2 with ground state atomie oxygen, ie

$$N_2(X,v\geq 12) + O(^3P) \rightarrow NO + N(^4S) \qquad (2)$$

where $N_2(X,v\geq 12)$ is formed by eollisional queneling of as N_2 ($A\ ^3\Sigma$)

$$N_2\ (A\ ^3\Sigma) + O_2 \rightarrow N_2(X,v) + O_2(b\ ^1\Sigma) \qquad (3)$$

The predietions of this "N_2 (X,v)" model are shown in Fig. 8.

Figures 9 and 10 summarize results in φ=0.5 methane/air (Fig 9) and ethylene/air (Fig 10) mixtures, where experimental data is compared with the baseline and N_2 (X,v) models (proeess(2)), as well as a third model,

$$N(^4S) + O_2(b^1\Sigma) \rightarrow NO + O(^3P) \qquad (4)$$

where $O_2(b^1\Sigma)$ is formed via proeess (3), above. It can be seen that for both fuel/air mixtures, the $O_2(b^1\Sigma)$ provides better agreement with the experimental data, although in both eases the predietions of the $O_2(b^1\Sigma)$ and N_2 (X,v) models are quite similar. Note also that the experimental results for φ=0.5 methane/air are quite similar to that for pure air, whereas peak NO produetion in φ=0.5 ethylene/air is lower by a faetor of ~two.

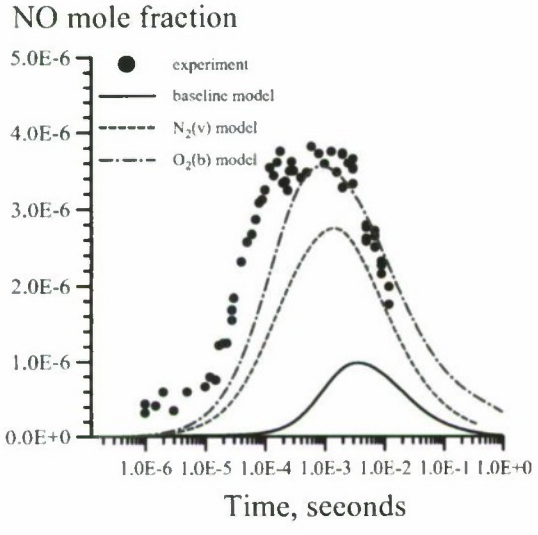

Figure 9. NO eoncentrations after a single-pulse discharge in methane-air for the three models used. P=60 torr, equivalence ratio φ=0.5, pulse energy 1.0 mJ.

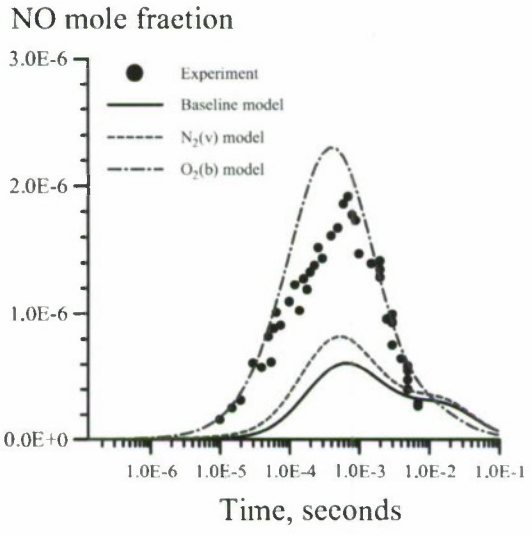

Figure 10. NO eoncentrations after a single-pulse discharge in ethylene-air for the three models used. P=60 torr, equivalence ratio φ=0.5, pulse energy 1.0 mJ.

This work is deseribed in more detail in Publieations 4 and 12.

iv. Pure rotational Coherent Anti-Stokes Raman Spectroscopy (CARS) studies of oxidation, heat release, and ignition in hydrogen-air nanosecond pulsed discharges.

Furthering our understanding of plasma assisted hydrogen/air combustion is clearly important due to its potential utility for application to future high speed (ie SCRAMJET) propulsion systems. Its inherent simplicity also makes it an ideal platform for PAC code development and validation. During the final year of the three year program of research summarized in this report, a significant effort has gone into studies of hydrogen/air PAC including: (i), Experimental CARS measurements of oxidation and heat release, (ii), hydrogen/air plasma-chemical code development, and (iii), hydrogen/air PAC sensitivity analysis. Each of these elements will be summarized below.

Hydrogen/Air Plasma-Chemical Model Development

The new hydrogen/air plasma-chemical code is described in detail in Zuzeek, et al., 2010 (Pub 14) and will be briefly summarized here. The nanosecond discharge portion of the model is patterned after that used previously for air, methane-air, and ethylene-air discharges (Topics i-iii, above). Briefly, the present model incorporates a nonequilibrium air plasma chemistry model developed by Kossy, et al [4], expanded to include hydrogen dissociation processes in the plasma, and the hydrogen-oxygen chemistry model (22 reactions among H, O, OH, H_2, O_2, H_2O, HO_2, and H_2O_2) developed by Popov [5]. Species concentration equations are coupled with the two-term expansion Boltzmann equation for the energy distribution function of plasma electrons, with electron impact cross sections taken from the literature. The full list of air plasma processes incorporated into the model and their rates is given in a Publication 3. The model also incorporates results from a new, first principles model describing energy coupling to the plasma from nanosecond discharge pulses, which will be described separately under program element v, below, and quasi-one-dimensional conduction heat transfer, which for the cases to be discussed in the findings section assumes a constant wall temperature boundary condition of T_w = 300 K. This boundary condition can be modified as appropriate.

Experimental CARS Results

Figures 11 and 12 summarize the most important finding in hydrogen-air mixtures. Figure 11 is analogous to Fig. 5, showing experimental CARS temperatures as a function of number of pulses in a 40 kHz burst in 40 Torr of air, and hydrogen-air at a variety of equivalence ratios, along with modeling predictions. Unlike Fig. 5, however, Fig. 11 shows that at burst durations in the approximate range 16 – 20 msec (640 – 800 pulses) the experimental temperatures, as well as the model predictions, for both φ = 0.5 and φ =1 exhibit a distinct maximum, and then decay. Furthermore, as shown in Fig. 12, the O_2 mole fractions for the stoichiometric mixture, obtained from the Sandia CARS fitting code used for inference of rotational temperature from the experimental CARS spectra and which floats this parameter, decreases very rapidly in the region of 15 - 20 msec duration bursts. Figure 12 also shows that O_2 mole fraction decay agrees well with the plasma kinetic model predictions. The observed temperature maximum, coupled with the observed rapid loss in O_2, is a strong indication that ignition has occurred in these mixtures.

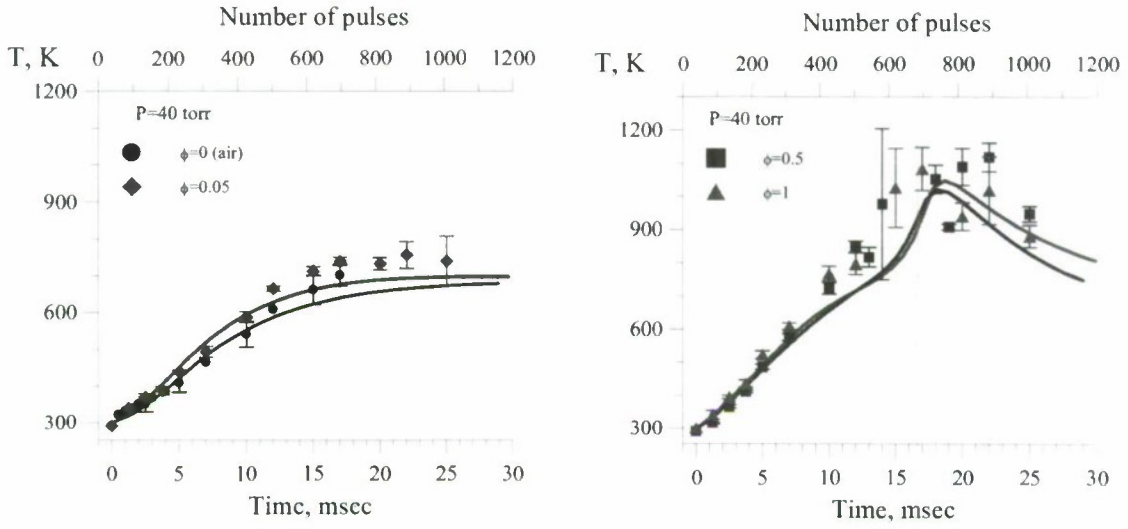

Figure 11: Comparison of experimental centerline (CARS) temperatures in a repetitively pulsed nanosecond discharge operated in repetitive burst mode in air and in hydrogen-air at ϕ=0.05, 0.5, and 1.0 at P=40 Torr with plasma chemistry kinetic model predictions. Pulse repetition rate is ν=40 kHz, burst repetition rate 10 Hz.

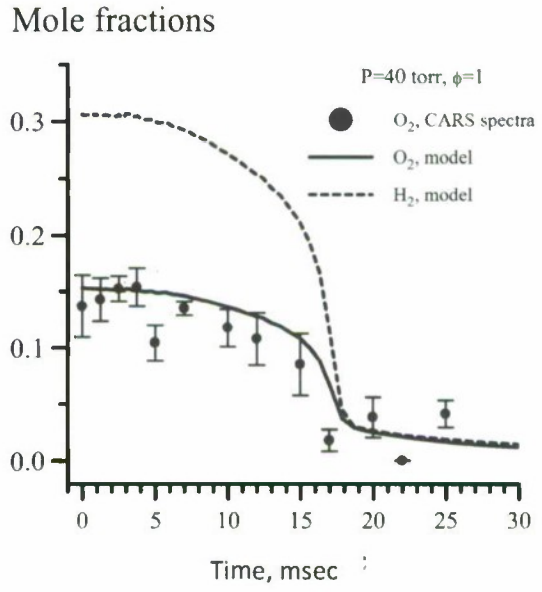

Figure 12: Oxygen mole fraction inferred from CARS synthetic spectra for hydrogen-air at the conditions of Fig. 4 (for ϕ=1.0). Also shown are hydrogen and oxygen mole fractions predicted by a plasma chemical kinetic model for the same conditions. Oxygen depletion during plasma chemical oxidation / ignition is apparent.

Sensitivity Analysis

In addition to hydrogen/air PAC code validation summarized, an extensive sensitivity analysis has been performed, which is described in detail in Zuzeek, et al (2010) and Bowman, et al. (2010). Summarizing the results of that analysis, very briefly, it is found that for single discharge pulse oxidation, initial low temperature heating, in excess of that resulting from direct energy input from the discharge, is controlled primarily by the following sequence of three processes, all of which are relatively rapid at 300 K,

$$H + O_2 + M \rightarrow HO_2 + M \quad (5)$$
$$O + HO_2 \rightarrow OH + O_2 \quad (6)$$
$$OH + H_2 \rightarrow H + H_2O \quad (7)$$

Note that under these highly non-equilibrium conditions, where atomic oxygen is formed in much higher quantities than in low temperature equilibrium combustion, the three body recombination process (5) actually acts as a source of OH and subsequent heat release, as opposed to a radical sink. At intermediate temperatures, 500 – 600 K, the rate of fuel oxidation increases significantly, primarily due to four additional reactions controlling chain branching,

$$H + HO_2 \rightarrow H_2O + O \quad (8)$$
$$H + HO_2 \rightarrow OH + OH \quad (9)$$
$$H + HO_2 \rightarrow H_2 + O_2 \quad (10)$$
$$O\ (^3P) + H_2 \rightarrow H + OH. \quad (11)$$

Figures 13 and 14 summarize findings for burst mode oxidation, heating and ignition. Figure 13 compares predicted temperature rise for the conditions of Fig. 11 (at φ=1) for the full plasma kinetic model (solid curve) and a reduced chemistry set that includes processes (5) – (11) above, plus the following additional two,

$$H + O_2 \rightarrow O + OH \quad (12)$$
$$OH + HO_2 \rightarrow H_2O + O_2 \quad (13)$$

It can be seen that the predictions are essential identical. Figure 14 is analogous to Fig. 13, but shows the temporal evolution of key species during burst mode oxidation/ignition predicted by the full (left) and reduced (right) chemical model. It is again found that the two sets of predictions are essentially identical.

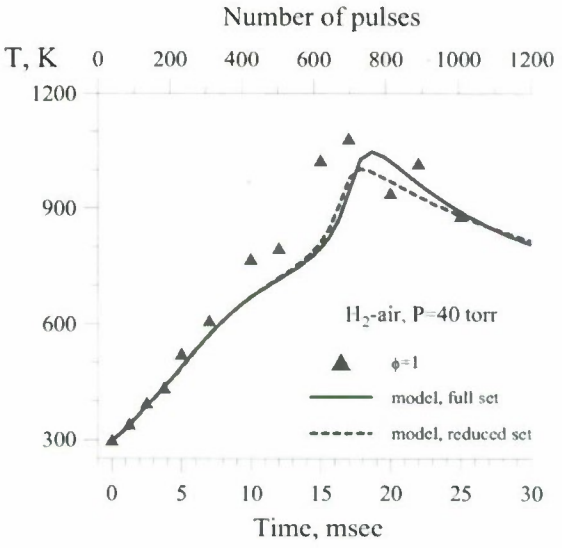

Figure 13: Temperature during H_2-air oxidation/ignition in burst mode at ν=40 kHz, predicted by full and reduced reaction sets. H_2-air, ϕ=1, P=40 torr, initial temperature T=300 K. CARS temperatures shown for comparison.

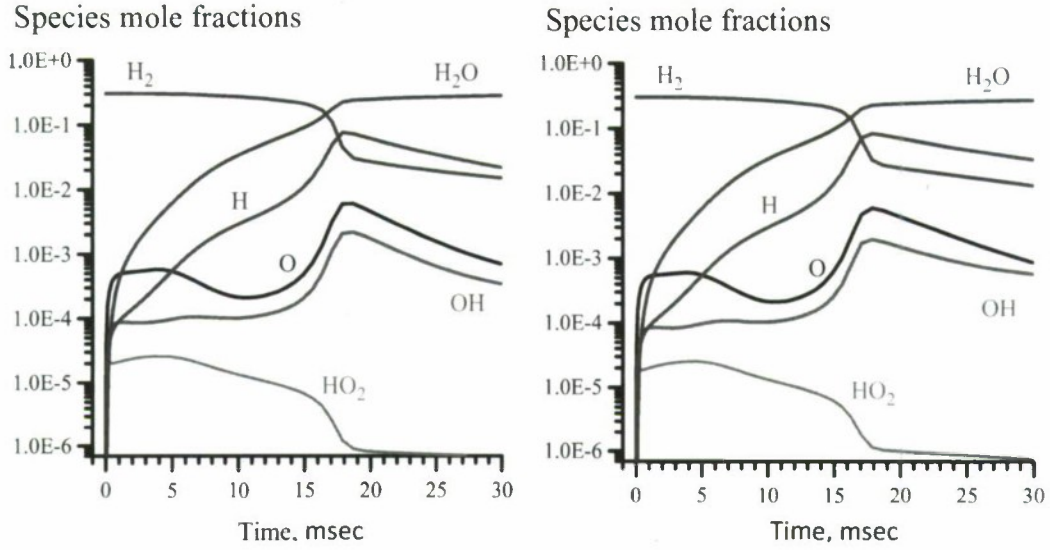

Figure 14: Species mole fractions during burst mode hydrogen-air oxidation/ignition, predicted by a plasma chemical kinetic model at the conditions of Fig. 13. Full reaction set (left) and reduced set (right).

Note that the results summarized above are presented in more detail in Publications 15 and 16. A manuscript has also been submitted to the 2010 International Symposium on Combustion, to be held in Beijing, China in August of 2010 (Publication 8).

v. Development of a new, non-empirical model for nanosecond pulsed discharge plasma dynamics and energy coupling.

Nanosecond pulsed discharge modeling has focused on two closely related problems, (a) The temporal dynamics of nanosecond pulsed discharge development and (b) Energy coupling to the plasma as a function of heavy species density, which varies with discharge pulse number when operating in burst mode. Both analytic and numeric models have been developed, some principal results of which are summarized below. Full details are provided in Publication 7.

Figure 15 illustrates the one-dimensional geometry that is used for the discharge model. Referring to Fig. 1, the discharge section can be modeled as a pair of electrodes, separated by distance L = 1 cm, covered with a dielectric layer with dielectric permeability ε (the quartz channel). As illustrated in Fig. 16, the applied voltage is assumed to have a Gaussian temporal distribution with full width at half maximum of ~25 nsec and peak voltage of ~18 kV. Skipping the details, the model predicts that during the initial stage of the

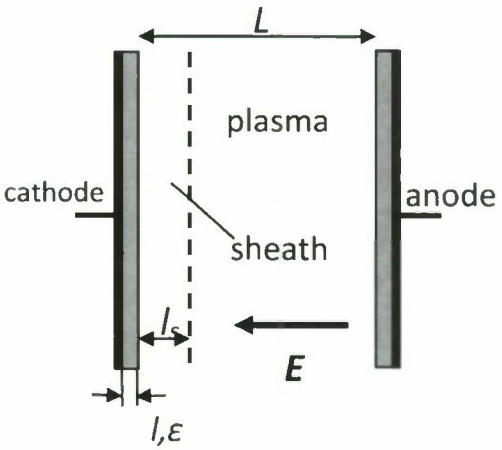

Figure 15. Schematic of the discharge model geometry

pulse, when the applied voltage is less than the breakdown voltage, the electric field between the electrodes is uniform, equal to V_{app}/L. When the applied voltage achieves breakdown (at ~88 nsec in Fig. 16), a high field sheath (of thickness $l_s \sim 1$ mm) rapidly forms in the vicinity of the cathode. Simultaneously the electric field within the "plasma" drops rapidly, to ~10% of the applied voltage. In essence, after breakdown, nearly the entire applied voltage is dropped across the sheath region. Figure 16 (left) shows that with the exception of the small dip in the numerical model at the point of breakdown, the analytic and numeric solutions are essentially identical.

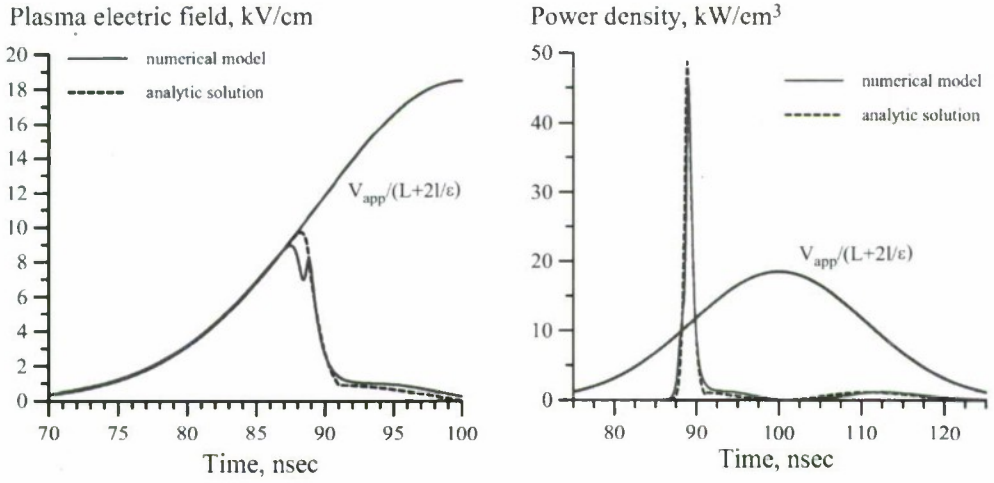

Figure 16. Comparison of time-dependent electric field (left) and coupled power (right) in the plasma predicted by numerical and analytic discharge models, along with applied voltage waveform.

As can be seen in Fig. 16 (right), the majority of the energy coupled to the plasma occurs in a narrow time window (~1-2 nanoseconds) during breakdown. More quantitatively, the model predicts that the energy coupled to the plasma during the pulse is limited primarily by charge accumulation on the dielectric surfaces covering the electrode plates. Basically, the coupled pulse energy, Q_{cap}, is

$$Q_{cap} \approx \frac{1}{2} C_{total} V_0^2 = \frac{1}{2} \frac{\varepsilon_0 \varepsilon A}{2l} V_0^2 \qquad (12)$$

where C_{total} is the total capacitance of the charged dielectric plates, ε is the dielectric permeability, A is the electrode surface area, l is the dielectric plate thickness, and V_0 is breakdown voltage. Note that since breakdown voltage in the plasma predicted by the model, V_0=8-10 kV at the conditions of the present experiments, is significantly lower than the peak pulse voltage applied to the electrodes, V_{app}=20 kV (Fig. 16 left), the coupled pulse energy is only ~15-25% of the maximum energy stored in the capacitance of the load. The remainder is reflected back to the power supply when the pulsed voltage is reduced to zero. It can be seen that the pulse energy coupled to the plasma can be significantly increased if the thickness of the dielectric layers is reduced.

The new model provides a theoretical foundation for predicting totaled coupled pulse energy as a function of pulse number in a pulse burst. It is shown in publication 6 that the totaled coupled energy per molecule is approximately constant, so that

$$q_{pulse} \approx \frac{1}{2}\frac{\varepsilon\varepsilon_0 V_0^2}{2lL}\frac{1}{Ne} \approx 0.28 \text{ meV / molecule} \qquad (13)$$

In other words, as the temperature increases during a burst (at constant pressure), the number density of the plasma drops, resulting in a linear drop of total coupled pulse energy with temperature. Physically this occurs because the drop in density results in a drop in breakdown voltage, reducing the total coupled pulse energy according to (12).

References

[1] Niemi K., Gathen V. S. and H F Dobele H. F., Plasma Sources Sci. Technol. **14,** p. 375 (2005).

[2] Niemi, K, Gathen, S. V., and Doebele, H.F. ,J. Phys. D **34**, p. 2330 (2001).

[3] Bromly, J.H., Barnes, F.J., Mandyezewsky, R., Edwards, T., and Haynes, B., 24th Symp. (Int) Comb., (The Combustion Institute, Pittsburgh, 1992).

[4] I.A. Kossyi, A.Y. Kostinsky, A.A. Matveyev, and V.P. Silakov, Plasma Sources Sci. Technol. **1**, p. 207 (1992)

[5] Popov, NA, Plasma Physics Reports **34,** p. 376 (2008).

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Publications

Refereed Journal Papers

1. I.V. Adamovich, W.R. Lempert, J.W. Rich, and Y. G. Utkin, "Repetitively Pulsed Nonequilibrium Plasmas for Magnetohydrodynamic Flow Control and Plasma-Assisted Combustion", **Journal of Propulsion and Power**, vol. 24, No. 6, 2008, pp. 1198-1215
2. M. Uddi, N. Jiang, E. Mintusov, I. V. Adamovich, and W. R. Lempert "Atomic Oxygen Measurements in Air and Air/Fuel Nanosecond Pulse Discharges by Two Photon Laser Induced Fluorescence, Proceedings of the Combustion Institute, vol. 32, pp. 929-936, 2009.
3. E. Mintusov, A. Serdyuchenko, I. Choi, W.R. Lempert, and I.V. Adamovich , "Mechanism of Plasma Assisted Oxidation and Ignition of Ethylene-Air Flows by a Repetitively Pulsed Nanosecond Discharge", Proceedings of the Combustion Institute, vol 32, pp. 3181-3188, 2009.
4. M. Uddi, N. Jiang, I. V. Adamovich, and W. R. Lempert, "Nitric Oxide Density Measurements in Air and Air/Fuel Nanosecond Pulse Discharges by Laser Induced Fluorescence," J. Phys. D:Appl. Phys., 42, 075205 2009.
5. Y. Zuzeek, I. Choi, M. Uddi, I.V. Adamovich, and W. R. Lempert, "Pure Rotational CARS Thermometry Studies of Low Temperature Oxidation Kinetics in Air and Ethylene-Air Nanosecond Pulse Discharge Plasmas," Accepted for publication in J. Phys. D: Appl. Phys, December, 2009.
6. I.V. Adamovich, I. Choi, N. Jiang, J.-H Kim, S. Keshav, W.R. Lempert, E. Mintusov, M. Nishihara, M. Samimy, and M.Uddi, "Plasma Assisted Ignition and High-Speed Flow Control: Non-Thermal and Thermal Effects," Plasma Sources Science and Technology, vol. 18, 2009, p. 034018.
7. I.V. Adamovich, M. Nishihara, I. Choi, M. Uddi, and W.R. Lempert, "Energy Coupling to the Plasma in Repetitive Nanosecond Pulse Discharges", Physics of Plasmas, vol. 16, 2009, p. 113505.
8. Y. Zuzeek, S. Bowman, I. Choi, I.V. Adamovich, and W.R. Lempert, "Pure Rotational CARS Studies of Thermal Energy Release and Ignition in Nanosecond Repetitively Pulsed Hydrogen-Air Plasmas," submitted to the 2010 International Symposium on Combustion, Beijing, China, August, 2010.

Refereed Conference Proceedings

9. M. Uddi, N. Jiang, K.Frederickson, E. Mintusov, I. V. Adamovich, and W. R. Lempert, Oxygen Atom Measurements in a Nanosecond Pulse Discharge by Two Photon Absorption Laser Induced Fluorescence," AIAA Paper #2007-4027, 38th Plasmadynamics & Lasers Conference, Miami, FL, 25-28 June, 2007.
10. M. Uddi, N. Jiang, E. Mintusov, I. V. Adamovich, and W. R. Lempert, "Atomic Oxygen Measurements in Air and Air/Fuel Nanosecond Pulse Discharges by Two Photon Laser Induced Fluorescence," AIAA Paper 2008-1110 , 46th Aerospace Sciences Meeting and Exhibit, 7-10 January 2008, Reno, NV.
11. E. Mintusov, A. Serdyuchenko, I. Choi, W.R. Lempert, and I.V. Adamovich, "Mechanism of Plasma Assisted Oxidation and Ignition of Ethylene-Air Flows by a Repetitively Pulsed Nanosecond Discharge", AIAA Paper 2008-1106, 46th Aerospace Sciences Meeting and Exhibit, 7-10 January 2008, Reno, NV.

12. M. Uddi, N. Jiang, I. V. Adamovich, and W. R. Lempert, "Nitric Oxide Density Measurements in Air and Air/Fuel Nanosecond Pulse Discharges by Laser Induced Fluorescence," AIAA-2008-3884, 39 Plasmadynamics and Lasers Conference, 23-26 June 2008, Seattle, WA.

13. I. Choi, M. Uddi, Y. Zuzeek, I.V. Adamovich, and W.R. Lempert, "Stability and Heating Rate of Air and Ethylene-Air Plasmas Sustained by Repetitive Nanosecond Pulses", AIAA Paper 2009-0688, 47th Aerospace Sciences Meeting and Exhibit, 5-8 January 2009, Orlando, FL.

14. Yvette Zuzeek, Aaron Montello, Inchul Choi, Munetake Nishihara, Igor V. Adamovich, and Walter R. Lempert, "Energy Coupling and Heat Release in Air and Ethylene-Air Nanosecond Pulse Discharge Plasmas," AIAA-2009-3591, 40th AIAA Plasmadynamics and Lasers Conference, 22-25 June 2009 / San Antonio, TX.

15. Y. Zuzeek, S. Bowman, I. Choi, I. Adamovich, and W. Lempert, "Pure Rotational CARS Measurements of Thermal Energy Release and Ignition in Nanosecond Pulse Burst Air and Hydrogen-Air Plasmas," AIAA-2010-648, 48th AIAA Aerospace Sciences Meeting, 4-7 January, 2010, Orlando, FL.

16. S. Bowman, I. Choi, I. Adamovich, and W. Lempert, "Kinetics of Low-Temperature Hydrogen Oxidation and Ignition by Repetitively Pulsed Nonequilibrium Plasmas," AIAA-2010-1590, 48th AIAA Aerospace Sciences Meeting, 4-7 January, 2010, Orlando, FL.

Oral Presentations

1 W. Lempert and I. Adamovich, "Atomic Oxygen Measurements in Nanosecond Pulse Discharges by Two Photon Laser Induced Fluorescence," Invited Talk (given by W. Lempert), Workshop on Fundamentals of Aerodynamic Flow and Combustion Control by Plasmas, Varenna, Italy, May 28th, 2007.

2 I.V. Adamovich, W.R. Lempert, and J. W. Rich, "Repetitively Pulsed Nonequilibrium Plasmas for Plasma-Assisted Combustion, High-Speed Flow Control, and Molecular Lasers", invited lecture (given by I. Adamovich) at the Aerospace Thematic Workshop "Fundamentals of Aerodynamic Flow and Combustion Control by Plasmas", May 28-31, 2007, Varenna, Italy.

3 M. Uddi, I. Choi, E. Mintoussov, N. Jiang, I. Adamovich, and W. Lempert, "Spatially and Temporally Resolved Atomic Oxygen Measurements in Short Pulse Discharges by Two Photon Laser Induced Fluorescence," 60th APS Gaseous Electronics Conference, Crystal City, VA, October 2nd, 2007.

4 E. Mintoussov, A. Bao, W. Lempert, and I. Adamovich, "Pulsed Nanosecond Discharge Development and Production of Active Particles," 60th APS Gaseous Electronics Conference, Crystal City, VA, October 2nd, 2007.

5 W. Lempert, invited talk, "Optical diagnostic studies of high speed and plasma aerodynamic flows," Dept of Aeronautical Engineering, University of Illinois -Urbana Champaign, February 18th, 2008.

6 W. Lempert, invited talk, "Kinetic studies of low temperature non-equilibrium weakly ionized air plasmas" University of Wisconsin – Madison, Department of Plasma Physics, April 21, 2008.

7 I.V. Adamovich, W.R. Lempert, J.W. Rich, and M. Samimy, "Experimental Studies of High-Speed Flow Control and Ignition by Nonequilibrium Plasmas", invited lecture at 19th Europhysics

Conference on the Atomic and Molecular Physics of Ionized Gases (ESCAMPIG XIX), 15-19 July 2008, Granada, Spain

8 W. R. Lempert, invited talk, "Optical measurements in plasmas and nonequilibrium flows," von Karman Institute for Fluid Dynamics Workshop, *Non-Equilibrium Gas Dynamics, from Physical Models to Hypersonic Flights,* Sept 8-12, 2008.

9 W. Lempert, M. Uddi, and I. Adamovich, Laser Induced Fluorescence Studies of NO Kinetics in Short Pulse Air and Air-Fuel Nonequilibrium Discharges, GEC08-2008-000178, 53rd APS Gaseous Electronics Conference, Dallas, TX 13-17 October, 2008.

10 W. Lempert, invited talk, "Optical diagnostic studies of high speed and plasma acrodynamic flows," Department of Aerospace Engineering and Engineering Mechanics, University of Texas – Austin, March 26th, 2009.

11 W. Lempert , M. Uddi , I. Choi , Y. Zuzeek, M. Webster, N. Jiang, I. Adamovich, invited talk, "Optical diagnostic studies of non-equilibrium plasmas and high speed flows," 8th Workshop on Frontiers in Low Temperature Plasma Diagnostics, Blansko, Czech Republic, April 21, 2009.

12 Y. Zuzeek, A. Montello, I. Choi, M. Uddi, I.V. Adamovich, and W.R. Lempert, "Rate of Thermal Energy Relcase in Nanosecond Pulse Burst Air and Ethylene-Air Plasmas", 19th International Symposium on Plasma Chemistry (ISPC), Bochum, Germany, 27-31 July 2009.

Interactions

1.	Svetlana Starikovskaya:	Ecole Polytechnic, FR
2.	Andrey Starikovskiy	Drexel University
3.	Sergey Leonov:	Joint Institute of High Temperature, Moscow
4.	Sergey Macheret:	Lockheed Martin
5.	Boris Potapkin	Moscow State University

Inventions - None